

Macroscopic characterization and phenomenological modeling of thermally-responsive shape memory polymers

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Abstract

The rational design of shape memory polymer based adaptive structures requires a comprehensive examination of these materials under general multiaxial stress and strain states. This is also necessary for the identification of response functions and the evaluation of predictive capabilities of theoretical models proposed in the literature for this class of smart materials. In this paper we discuss different testing procedures and related methods of data analysis that furnish a firm experimental basis for the evaluation of functional properties of shape memory polymers (SMPs). Moreover, two broad classes of models are discussed, thermoelastic models used in the analysis of rate independent problems and thermo-viscoelastic models, which account for time effects typical for polymer materials. It is shown that the tensor-valued response functions of the general three-dimensional theory presented in this paper may be determined directly from strain/stress storage/recovery profiles measured in strain-controlled shape memory cycles performed in different deformation modes. Finally, the influence of thermo-temporal conditions on functional properties of SMPs is shortly discussed with the view of the evaluation of different classes of these materials and the corresponding theoretical models.

1. INTRODUCTION

There are many examples of adaptive structures from a broad range of engineering and medical applications [1 - 5], but much of the earlier development has been related to the parallel research on the shape memory alloys (SMAs). Only somewhat later it was realized that shape memory polymers (SMPs) show great promise in the development of adaptive structures. However, before such applications can be attempted, the thermo-mechanical behavior and functional properties of these smart materials must be thoroughly tested and theoretically modeled in the general multi-axial strain and stress states.

The functional properties (shape fixity, shape recovery, etc.) of shape memory polymers, including shape memory polymer nanocomposites, are experimentally studied by different shape memory cycle procedures [5 - 8]. In addition, there is a wide range of testing techniques available to characterize the thermo-viscoelastic behavior of SMPs (e.g. standard creep and relaxation tests, the dynamical mechanical analysis, etc.). Moreover, all these tests may be performed in various deformation modes such as uniaxial

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tension, compression, bending or torsion. These differing experimental methods and testing protocols have resulted in a great variety of the reported data making the evaluation of the shape memory performance under different thermo-temporal conditions somewhat difficult. For example, there are no clear interrelations between shape fixity, shape recovery, and other functional properties determined in uniaxial tension and bending or torsion tests for seemingly the same SMP. Moreover, most of the data available in the open literature were obtained in the one-axis, single deformation mode experiments such as uniaxial tension or compression with only axial strain measured. In this respect, it has to be emphasized that the rational design of SMP-based adaptive structures requires a comprehensive examination of these smart materials under general multi-axial stress and strain states in different deformation modes. This is also necessary for the identification of response functions and the evaluation of predictive capabilities of the theoretical models proposed in the literature.

In this paper we discuss different testing procedures that are needed to assess the functional properties of SMPs under general three-dimensional (3D) strain and stress states, and a necessity of such 3D data to identify the response functions and to calibrate involved material parameters in various constitutive models proposed in the literature for this class of smart materials (see review articles [8, 9]). Two broad classes of models are considered, thermoelastic [10 - 12] and thermo-viscoelastic theories [13, 14]. It is shown that for certain classes of theoretical models, the relevant response functions may be determined directly from strain/stress storage/recovery profiles measured in strain-controlled shape memory cycles. This study provides an extension of the main results obtained in our paper [15] to the general 3D case including different deformation modes. Finally, the influence of thermo-temporal conditions on functional properties of SMPs is shortly discussed with the view of the evaluation of different theoretical models.

2. DIFFERENT TYPES OF SHAPE MEMORY CYCLES

Different types of SMPs (amorphous, semicrystalline, etc.), their various functional properties (dual and multiple shape memory effects, one- and two-way shape memory property, temperature memory effect, etc.), different kinds of stimuli (temperature, light, etc.) as well as physical mechanisms responsible for a macroscopic behavior of these polymer materials have been discussed in the literature (see [2 - 8] and references cited therein) and will not be repeated here.

Most of thermally induced SMPs are dual-shapes with one-way shape memory property. The functional properties of such SMPs are quantified in multiple-step cyclic thermomechanical tests (see Figure 1) referred to as shape memory cycles (SMCs). As described in [2 - 8], each cycle involves programming of a sample (Steps 1 - 3), that is, the creation of a temporary shape and the recovery of a permanent shape or restoring stress (Step 4a or Step 4b, depending on the type of constraints). These four steps are preceded by the Step 0 if the deformation temperature is different from the high temperature. In effect, there are four basic types of SMCs. Moreover, programming and recovery cycles can be repeated several times with different temporary shapes in subsequent cycles. Furthermore, depending on the instrument used in experiment, these tests can be performed either in strain- or in stress-controlled modes such as uniaxial tension, shearing or bending. Accordingly, the strain and stress in Figure 1 should be understood in the generalized sense of mechanics, e.g. as the standard uniaxial strain and stress in the case of uniaxial tension or compression, or as a torsion angle and the associated twist couple in the case of simple torsion. In multiaxial tests, the strain and stress in Figure 1 should be understood as the second-order symmetric tensors. This interpretation refers also to all quantities specified as test parameters and quantities measured in the respective SMCs illustrated in Figure 1. The different types of SMCs generate slightly different and complementary data that are needed for both the characterization of the shape memory behavior of SMPs and the constitutive modeling of these materials.

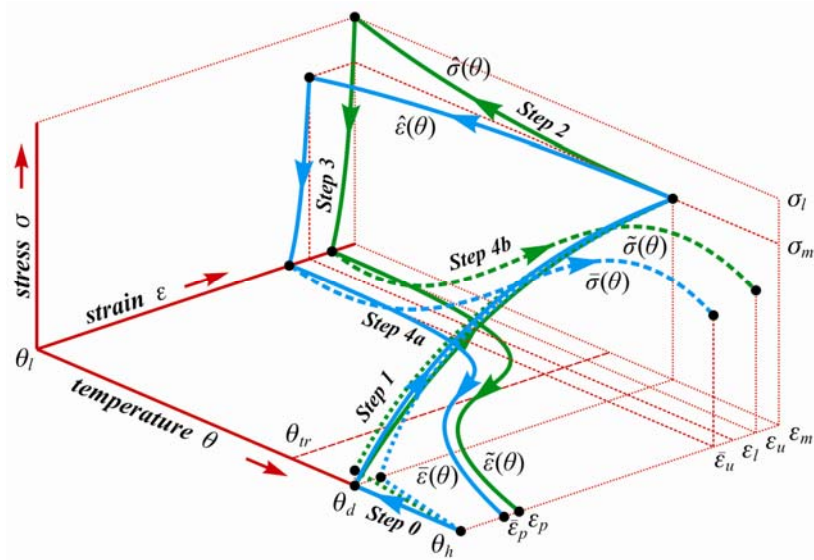


Figure 1. One-way shape memory cycles with differing high and deformation (programming) temperatures represented as single curve in 3D strain-stress-temperature space: Strain-controlled (green curves) and stress-controlled (blue curves) programming module followed by either unconstrained (solid lines) or constrained (interrupted lines) recovery process.

The basic test parameters defining SMCs consist of the high, low, and deformation temperatures, θ_h , θ_l and θ_d , respectively, and the maximum strain ε_m or stress σ_m depending on the control parameter. The ability of a particular SMP to fix a temporary shape and to restore a permanent (original) shape is quantified by the shape fixity (also called the strain fixity ratio) R_f and the shape recovery (also called the strain recovery ratio) R_r , which are defined (see [2 - 8]) in terms of strains ε_m , ε_u , ε_p and ε_l , $\bar{\varepsilon}_u$, $\bar{\varepsilon}_p$, respectively, measured in the corresponding SMCs (Figure 1). The quantitative analysis of both the shape fixity and recovery is a major concern in the development of shape memory polymers for specific applications. However, for the formulation of constitutive models of SMPs and for the calibration of the respective material parameters, it is necessary to measure the complete strain/stress storage/recovery profiles for different values of pre-strain ε_m (or pre-stress σ_m) besides the stress-strain relations at high and lower temperature. Moreover, all these tests should be performed for different deformation modes in order to quantify the functional properties of a particular SMP under general loading conditions.

3. 3D LINEAR THERMOELASTIC THEORY OF SMPs

The phenomenological constitutive models for thermally-responsive SMPs may be grouped in two broad classes referred to as thermoelastic and visco-thermoelastic models, respectively. Both classes may further be divided into subclasses depending on the range of admitted strains (small or finite). A review of various constitutive models may be found in [8, 9, 15]. Owing due to the complex thermomechanical behavior of SMPs, the advanced models usually involve a large number of material parameters (typically 15-30). For the calibration of these parameters, it is necessary to conduct multi-step experiments, which are both expansive and time-consuming. Moreover, the identification of response functions in the general

three-dimensional (3D) case is problematic. Therefore, it is highly required to develop simple models containing a limited number of well-defined constitutive functions and material parameters that can be easily identified experimentally.

A relatively simple (rate-independent) model based on the Linear Thermoelastic (LTE) theory has been developed by Liu et al. [10] who described SMP as a composite material where two phases coexist in the temperature range that defines the glass transition. Subsequently, this approach has been extended and refined by Chen and Lagoudas [11] and more recently by Gilormini and Diani [12]. For the one-dimensional case (uniaxial deformation), all these models may be unified into a single theory [15]. In this paper the formulation and analysis presented in [15] is extended to the general 3D LTE theory without any reference to the two-phase structure of SMPs used in [10-12].

Any constitutive theory for thermally-responsive SMPs must relate the strain history $\boldsymbol{\varepsilon}(t)$, stress history $\boldsymbol{\sigma}(t)$, and temperature history $\theta(t)$ for any time interval $[t_0, +\infty)$. Here $\boldsymbol{\varepsilon}$ and $\boldsymbol{\sigma}$ are symmetric second order strain and stress tensors, respectively, and t_0 denotes the initial time instant at which a material sample is in the stress and strain free state at a reference temperature θ_0 . Thus, the strain, stress, and temperature histories must satisfy the initial conditions $\boldsymbol{\varepsilon}(t_0) = \boldsymbol{\sigma}(t_0) = \mathbf{0}$ and $\theta(t_0) = \theta_0$. The formulation of LTE theory for shape memory polymers is based on the assumption that the total strain $\boldsymbol{\varepsilon}(t)$ at any time $t \in [t_0, +\infty)$ may be decomposed additively into the sum of the mechanical (elastic) strain $\boldsymbol{\varepsilon}_e(t)$, the thermal strain $\boldsymbol{\varepsilon}_\theta(t)$, and the so-called stored or frozen strain $\boldsymbol{\varepsilon}_s(t)$. With the linearity assumption applied to partial strains and the concept of storage process [10, 12], the 3D constitutive law of the linear thermoelastic theory takes the form (see also [11])

$$\boldsymbol{\varepsilon}(t) = \underbrace{\mathbf{C}(\theta(t))\boldsymbol{\sigma}(t)}_{\boldsymbol{\varepsilon}_e(t)} + \underbrace{\int_{t_0}^t \boldsymbol{\kappa}(\theta(s))\dot{\theta}(s)ds}_{\boldsymbol{\varepsilon}_\theta(t)} + \underbrace{\int_{t_0}^t \mathbf{D}(\theta(s))\boldsymbol{\sigma}(s)\dot{\theta}(s)ds}_{\boldsymbol{\varepsilon}_s(t)}. \quad (1)$$

Here the superimposed dot stands for the derivative with respect to time and s denotes the integration time, $t_0 \leq s \leq t$. Moreover, for the thermal and stored strains in integral terms in (1), the temperature history is understood as the net cooling history as defined in [11].

The constitutive law (1) involves three (tensor-valued) response functions, the second order symmetric thermal (expansion) tensor $\boldsymbol{\kappa}(\theta)$, the fourth order symmetric instant elastic compliance tensor $\mathbf{C}(\theta)$, and the fourth order symmetric distributed elastic compliance tensor $\mathbf{D}(\theta)$, each depending on temperature only. For the two-phase model [10 - 12], these response functions are given in terms of quantities characterizing the glassy and rubbery states of SMP. Various special theories in the class of LTE theory differ in the forms these response functions are assumed. In the general theory, it suffices to determine the response functions $\boldsymbol{\kappa}(\theta)$, $\mathbf{C}(\theta)$ and $\mathbf{D}(\theta)$ in an experimental program without any a priori assumption concerning the nature of SMP.

Without any reference to special models formulated in [10 - 12], it may be noted here that for an isotropic SMP, the response functions must be isotropic tensor functions of temperature. Accordingly, by the theorem on isotropic tensors, the response functions in the constitutive law (1) may be expressed in the form

$$\boldsymbol{\kappa}(\theta) = \alpha(\theta)\mathbf{I}, \quad \mathbf{C}(\theta) = L(\theta)\mathbf{I} - N(\theta)\mathbf{I} \otimes \mathbf{I}, \quad \mathbf{D}(\theta) = H(\theta)\mathbf{I} - M(\theta)\mathbf{I} \otimes \mathbf{I}. \quad (2)$$

Here \mathbf{I} and \mathbf{I} are the second order and fourth order unit tensors, respectively, $\alpha(\theta)$ is the thermal expansion coefficient and the physical meaning of the remaining response functions in (2) will be discussed below. Here it is enough to note that the form (2) of the response functions may be derived from the notion of symmetry developed within linear theory of thermoelastic materials.

4. TWO-PHASE MODELS

In the original formulation due to Liu et al. [10] and in the subsequent developments [11, 12], the shape memory polymer is considered as a composite material where two phases coexist in the temperature range that defines the glass transition. It is further assumed that the glassy or “frozen” phase with a volume fraction $\varphi(\theta)$ has the elastic behavior, which stems from internal energy, whereas the elastic behavior of the rubbery or “active” phase with a volume fraction $1 - \varphi(\theta)$ originates essentially from the entropy of macromolecular chains. Under these assumptions, the response functions in the general law (1) are assumed in the form derived from a simple mixture rule (see discussion in [12]). In particular, in the theory proposed by Chen et al. [11], the thermal tensor is given by

$$\boldsymbol{\kappa}(\theta) = (1 - \varphi(\theta))\boldsymbol{\kappa}_r(\theta) + \varphi(\theta)\boldsymbol{\kappa}_g(\theta). \quad (3)$$

Moreover, the response functions for the instant elastic compliance $\mathbf{C}(\theta)$ and the distributed elastic compliance $\mathbf{D}(\theta)$ are given by (Reuss average) and (incremental Reuss average) rules [11, 12]

$$\mathbf{C}(\theta) = (1 - \varphi(\theta))\mathbf{C}_r(\theta) + \varphi(\theta)\mathbf{C}_g(\theta), \quad \mathbf{D}(\theta) = \{\mathbf{C}_r(\theta) - \mathbf{C}_g(\theta)\} \frac{d\varphi(\theta)}{d\theta}. \quad (4)$$

In the constitutive relations (3) and (4), the subscripts g and r are used to indicate the respective quantities of the glassy and rubbery phase of a particular SMP. The expression (3) and (4)₁ for the elastic and thermal strain are identical to those in the model developed by Liu et al. [10]. However, the expression for the stored strain given in Eq. (4)₂ has some differences from theirs (see discussion in [11]).

For the two-phase model with both phases isotropic (see [10 - 12]), the use of rules (3) and (4) yields the following forms of the response functions appearing in the general definitions (2):

$$\alpha(\theta) = (1 - \varphi(\theta))\alpha_r(\theta) + \varphi(\theta)\alpha_g(\theta), \quad (5)$$

$$L(\theta) = \frac{(1 - \varphi(\theta))(1 + \nu_r(\theta))}{E_r(\theta)} + \frac{\varphi(\theta)(1 + \nu_g(\theta))}{E_g(\theta)}, \quad N(\theta) = \frac{(1 - \varphi(\theta))\nu_r(\theta)}{E_r(\theta)} + \frac{\varphi(\theta)\nu_g(\theta)}{E_g(\theta)}, \quad (6)$$

$$H(\theta) = \left\{ \frac{1 + \nu_r(\theta)}{E_r(\theta)} - \frac{1 + \nu_g(\theta)}{E_g(\theta)} \right\} \frac{d\varphi(\theta)}{d\theta}, \quad M(\theta) = \left\{ \frac{\nu_r(\theta)}{E_r(\theta)} - \frac{\nu_g(\theta)}{E_g(\theta)} \right\} \frac{d\varphi(\theta)}{d\theta}. \quad (7)$$

Here $\alpha_r(\theta)$ and $\alpha_g(\theta)$ are thermal expansion coefficients, $E_g(\theta)$, $\nu_g(\theta)$ and $E_r(\theta)$, $\nu_r(\theta)$ denote elastic moduli and Poisson’s ratios of the glassy and rubbery phases, respectively, all depending on temperature. With response functions (5) - (7), the general constitutive law (1) reduces to the form derived by Chen and Lagoudas [11]. These authors presented also a methodology different from that proposed in [10] to calibrate these response functions (for the 1D case) by using experimental data obtained by Liu et al [10]. The more general mixture rules than (3) and (4) have been used in [12] to determine the response functions for thermal expansion coefficients and elastic moduli. The comparison of the representative theoretical solutions derived in [10-12] with the data presented in [10] is shown in Figure 2. As may be seen in that figure, all these formulations of the two-phase LTE models predict the behavior of the tested shape memory polymer with reasonable accuracy, but no essential improvements are observed in comparison with the original formulation [10] (see [15] for more detailed discussion of this point). Keeping this in mind, a new methodology to identify the response functions in the general constitutive law (1) without any reference to the two-phase formulation is presented below.

The constitutive law (1) may be used to predict the behavior of SMPs under general 3D loading conditions whenever the constitutive functions have been determined. Alternatively, this law may serve to determine the response functions from SMCs performed in different deformation modes.

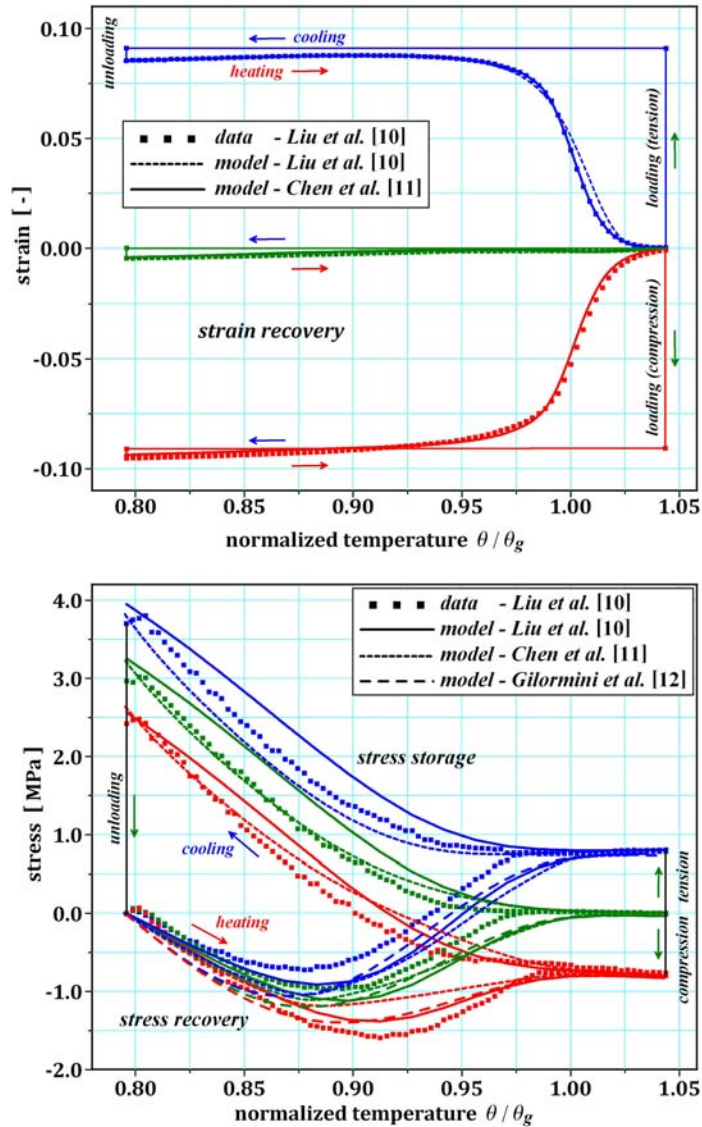


Figure 2. Strain recovery (above), stress storage and recovery (below) profiles for different pre-strains: Comparison of data and model predictions.

5. SIMULATION OF SHAPE MEMORY CYCLES

The general constitutive law (1) relates the strain, stress, and temperature history and serves for the determination of any one from given two others. In particular, when specified for the successive steps of

the strain-controlled SMCs (Fig. 1, green curves), this general constitutive law assumes the following special forms (see approach in [11, 15]):

Step 1 Loading at high temperature, $\theta = \theta_h$,

$$\boldsymbol{\varepsilon}(t) = \mathbf{C}(\theta_h)\boldsymbol{\sigma}(t), \quad 0 \leq t \leq t_h, \quad (8)$$

Step 2 Cooling in temperature range $\theta_h \geq \theta \geq \theta_l$ at fixed strain, $\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}_m$,

$$\boldsymbol{\varepsilon}_m = \mathbf{C}(\theta)\hat{\boldsymbol{\sigma}}(\theta) + \int_{\theta_h}^{\theta} \boldsymbol{\kappa}(\zeta)d\zeta + \int_{\theta_h}^{\theta} \mathbf{D}(\zeta)\hat{\boldsymbol{\sigma}}(\zeta)d\zeta, \quad \theta_h \geq \theta \geq \theta_l, \quad (9)$$

Step 3 Unloading at low temperature, $\theta = \theta_l$,

$$\boldsymbol{\varepsilon}(t) = \mathbf{C}(\theta_l)\boldsymbol{\sigma}(t) + \int_{\theta_h}^{\theta_l} \boldsymbol{\kappa}(\zeta)d\zeta + \int_{\theta_h}^{\theta_l} \mathbf{D}(\theta)\hat{\boldsymbol{\sigma}}(\theta)d\zeta, \quad t_l \leq t \leq t_u, \quad (10)$$

Step 4a Heating in temperature range $\theta_l \leq \theta \leq \theta_h$ at zero stress, $\boldsymbol{\sigma} = 0$,

$$\tilde{\boldsymbol{\varepsilon}}(\theta) = \int_{\theta_h}^{\theta} \boldsymbol{\kappa}(\zeta)d\zeta + \int_{\theta_h}^{\theta} \mathbf{D}(\zeta)\hat{\boldsymbol{\sigma}}(\zeta)d\zeta, \quad \theta_l \leq \theta \leq \theta_h, \quad (11)$$

Step 4b Heating in temperature range $\theta_l \leq \theta \leq \theta_h$ at fixed strain, $\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}_u$,

$$\boldsymbol{\varepsilon}_u = \mathbf{C}(\theta)\tilde{\boldsymbol{\sigma}}(\theta) + \int_{\theta_h}^{\theta} \boldsymbol{\kappa}(\zeta)d\zeta + \int_{\theta_h}^{\theta} \mathbf{D}(\zeta)\hat{\boldsymbol{\sigma}}(\zeta)d\zeta. \quad (12)$$

If the response functions $\boldsymbol{\kappa}(\theta)$, $\mathbf{C}(\theta)$ and $\mathbf{D}(\theta)$ are known or assumed, these laws for the successive steps of SMCs require the solution of the integral-differential equation, which may be reduced to the solution of the initial value problem for the first order ordinary differential equation.

The constitutive law (8) - (12) may be used in different way with far reaching implications. Under the assumption that the thermal strains during cooling and heating coincide, the constitutive laws for the Step 2, Step 4a and Step 4b yield the following relations

$$\mathbf{C}(\theta)\hat{\boldsymbol{\sigma}}(\theta) = \boldsymbol{\varepsilon}_m - \tilde{\boldsymbol{\varepsilon}}(\theta), \quad \mathbf{C}(\theta)\tilde{\boldsymbol{\sigma}}(\theta) = \boldsymbol{\varepsilon}_u - \tilde{\boldsymbol{\varepsilon}}(\theta), \quad (13)$$

and

$$\mathbf{D}(\theta)\hat{\boldsymbol{\sigma}}(\theta) = \frac{d\tilde{\boldsymbol{\varepsilon}}(\theta)}{d\theta} - \boldsymbol{\kappa}(\theta) = -\frac{d}{d\theta}(\mathbf{C}(\theta)\tilde{\boldsymbol{\sigma}}(\theta)) - \boldsymbol{\kappa}(\theta). \quad (14)$$

Keeping in mind that the thermal tensor $\boldsymbol{\kappa}(\theta)$ may be determined from the standard thermal tests for each kind of polymer [10 - 12], the relations (13) and (14) indicate that the response functions $\mathbf{C}(\theta)$ and $\mathbf{D}(\theta)$ of the LTE theory may be determined from the strain and stress profiles measured in the strain-controlled SMCs. For the one-dimensional case, the relevant results have been derived in [15]. Here it is shown that the same approach applies to the general 3D case and special deformation modes.

6. CALIBRATION OF RESPONSE FUNCTIONS AND EVALUATION OF MODELS

In the uniaxial tension / compression of an elongated uniform bar, the strain and stress tensors are

$$\boldsymbol{\varepsilon}(t) = \begin{bmatrix} \varepsilon(t) & 0 & 0 \\ 0 & \varepsilon_L(t) & 0 \\ 0 & 0 & \varepsilon_L(t) \end{bmatrix}, \quad \boldsymbol{\sigma}(t) = \begin{bmatrix} \sigma(t) & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}. \quad (15)$$

Here ε and σ are the axial strain and stress, respectively, ε_L is the lateral strains (equal in both lateral directions) while the lateral stresses are zero, $\sigma_L = 0$. For isotropic SMPs, the use of (15) in the general constitutive law (1) with the response functions defined in (2) gives two independent constitutive laws for axial and lateral strains, respectively. These constitutive laws may next be specified for the successive steps of the strain-controlled SMCs. In particular, constitutive laws for Step 2, Step 4a and Step 4b take the form

$$\begin{aligned} \varepsilon_m &= \{L(\theta) - N(\theta)\} \hat{\sigma}(\theta) + \int_{\theta_h}^{\theta} \alpha(\zeta) d\zeta + \int_{\theta_h}^{\theta} \{H(\zeta) - M(\zeta)\} \hat{\sigma}(\zeta) d\zeta, \\ \varepsilon_{mL} &= -N(\theta) \hat{\sigma}(\theta) + \int_{\theta_h}^{\theta} \alpha(\zeta) d\zeta - \int_{\theta_h}^{\theta} M(\zeta) \hat{\sigma}(\zeta) d\zeta, \end{aligned} \quad (16)$$

$$\begin{aligned} \tilde{\varepsilon}(\theta) &= \int_{\theta_h}^{\theta} \alpha(\zeta) d\zeta + \int_{\theta_h}^{\theta} \{H(\zeta) - M(\zeta)\} \hat{\sigma}(\zeta) d\zeta, \\ \tilde{\varepsilon}_L(\theta) &= \int_{\theta_h}^{\theta} \alpha(\zeta) d\zeta - \int_{\theta_h}^{\theta} M(\zeta) \hat{\sigma}(\zeta) d\zeta, \end{aligned} \quad (17)$$

$$\begin{aligned} \varepsilon_u &= \{L(\theta) - N(\theta)\} \tilde{\sigma}(\theta) + \int_{\theta_h}^{\theta} \alpha(\zeta) d\zeta + \int_{\theta_h}^{\theta} \{H(\zeta) - M(\zeta)\} \tilde{\sigma}(\zeta) d\zeta, \\ \varepsilon_{uL} &= -N(\theta) \tilde{\sigma}(\theta) + \int_{\theta_h}^{\theta} \alpha(\zeta) d\zeta - \int_{\theta_h}^{\theta} M(\zeta) \tilde{\sigma}(\zeta) d\zeta, \end{aligned} \quad (18)$$

respectively. The constitutive laws for Step 1 and Step 3 take the classical form of Hooke's Law at high and low temperature and need not to be discussed here. The constitutive equations (16) - (18) may also be obtained directly from the general laws (9), (11) and (12). For the 1D case, as discussed in [15], the constitutive relations derived in this way may next be used for different purposes. In particular, from (16) - (18), the following expressions for the response functions $L(\theta)$ and $N(\theta)$ of the general LTE theory for isotropic SMPs are obtained

$$\begin{aligned} L(\theta) - N(\theta) &= \frac{\varepsilon_m - \tilde{\varepsilon}(\theta)}{\hat{\sigma}(\theta)} = \frac{\varepsilon_m - \varepsilon_u}{\hat{\sigma}(\theta) - \tilde{\sigma}(\theta)} = \frac{\varepsilon_u - \tilde{\varepsilon}(\theta)}{\tilde{\sigma}(\theta)}, \\ N(\theta) &= -\frac{\varepsilon_{mL} - \tilde{\varepsilon}_L(\theta)}{\hat{\sigma}(\theta)} = -\frac{\varepsilon_{mL} - \varepsilon_{uL}}{\hat{\sigma}(\theta) - \tilde{\sigma}(\theta)} = -\frac{\varepsilon_{uL} - \tilde{\varepsilon}_L(\theta)}{\tilde{\sigma}(\theta)}. \end{aligned} \quad (19)$$

It follows that both response functions may be determined directly from the strain/stress storage/recovery profiles measured in the strain-controlled SMC. Moreover, this may be done using different measured profiles. The expressions for the response functions $H(\theta)$ and $M(\theta)$ also follow from (16) - (18) by taking the derivative with respect to the temperature

$$H(\theta) - M(\theta) = \frac{1}{\hat{\sigma}(\theta)} \left\{ \frac{d\tilde{\varepsilon}(\theta)}{d\theta} - \alpha(\theta) \right\}, \quad M(\theta) = -\frac{1}{\hat{\sigma}(\theta)} \left\{ \frac{d\tilde{\varepsilon}_L(\theta)}{d\theta} - \alpha(\theta) \right\}. \quad (20)$$

Noting that the thermal expansion coefficient $\alpha(\theta)$ may be obtained from an independent thermal test (see [10 - 12]), the derived relations (19) and (20) prove that the response functions of the general 3D theory for isotropic SMPs may be completely determined from strain and stress storage / recovery profiles measured in the strain controlled SMCs performed in the uniaxial tension mode provided that both axial and lateral strains are measured. These relations give also a physical interpretation of the response

functions $L(\theta)$, $H(\theta)$, $N(\theta)$ and $M(\theta)$ independently of any assumptions concerning the two-phase structure of SMPs. In effect, the phenomenological theory discussed in this paper may be applied to all SMPs, including semi-crystalline ones with melting temperature as the transition temperature.

The only problem with the use of the formulae (19) and (20) is that no measurements of lateral deformation were made in experiments conducted by Liu et al. [10], and no such data have been ever published. This limitation may be overcome by performing SMC tests on the same SMP in a different deformation mode, for example, in the simple shear. In this case, the strain and stress tensors take particularly simple form

$$\boldsymbol{\varepsilon}(t) = \begin{bmatrix} 0 & \gamma(t) & 0 \\ \gamma(t) & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad \boldsymbol{\sigma}(t) = \begin{bmatrix} 0 & \tau(t) & 0 \\ \tau(t) & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad (21)$$

where γ and τ are the shear strain and the corresponding shear stress, respectively. For isotropic SMPs, the use of (21) in the general constitutive law (1) with the response functions defined in (2) gives the constitutive law relating the history of shear strain $\gamma(t)$, shear stress $\tau(t)$ and temperature $\theta(t)$,

$$\gamma(t) = L(\theta(t))\tau(t) + \int_{t_0}^t H(\theta(s))\tau(s)\dot{\theta}(s)ds. \quad (22)$$

This constitutive law may next be specified for the successive steps of the strain-controlled SMCs performed in simple shear mode. In particular, the constitutive laws derived from (22) for Step 2, Step 4a and Step 4b take the form

$$\begin{aligned} \gamma_m &= L(\theta)\hat{\tau}(\theta) + \int_{\theta_0}^{\theta} H(\zeta)\hat{\tau}(\zeta)d\zeta, \\ \tilde{\gamma}(\theta) &= \int_{\theta_h}^{\theta} H(\zeta)\hat{\tau}(\zeta)d\zeta, \\ \gamma_u &= L(\theta)\tilde{\tau}(\theta) + \int_{\theta_h}^{\theta} H(\zeta)\tilde{\tau}(\zeta)d\zeta. \end{aligned} \quad (23)$$

Here $\hat{\tau}(\theta)$, $\tilde{\gamma}(\theta)$ and $\tilde{\tau}(\theta)$ are the shear stress storage, shear strain recovery, and shear stress recovery profiles measured in the respective steps of the strain-controlled SMCs (see Fig. 1). The inspection of the relations (23) shows that the response functions $L(\theta)$ and $H(\theta)$ may be determined directly from the measured profiles

$$L(\theta) = \frac{\gamma_m - \tilde{\gamma}(\theta)}{\hat{\tau}(\theta)} = \frac{\gamma_m - \gamma_u}{\hat{\tau}(\theta) - \tilde{\tau}(\theta)} = \frac{\gamma_u - \tilde{\gamma}(\theta)}{\tilde{\tau}(\theta)}, \quad H(\theta) = \frac{1}{\hat{\tau}(\theta)} \frac{d\tilde{\gamma}(\theta)}{d\theta}. \quad (24)$$

Having the response functions $L(\theta)$ and $H(\theta)$ determined from the relations (24), the remaining two response functions $N(\theta)$ and $M(\theta)$ may be determined from (19)₁ and (20)₁ with the axial strain measured only. This methodology is fairly straightforward but it requires that SMC tests are performed on the same polymer in the uniaxial and shear deformation modes.

The relations (19) and (24) may also be used to evaluate the applicability of the general LTE theory to particular classes of SMPs. For example, it follows from (19) that according to the LTE theory, different strain and stress profiles measured in SMCs are not independent but they must satisfy the following relations

$$(\varepsilon_u - \tilde{\varepsilon}(\theta))\hat{\sigma}(\theta) = (\varepsilon_m - \tilde{\varepsilon}(\theta))\tilde{\sigma}(\theta), \quad (\varepsilon_{uL} - \tilde{\varepsilon}_L(\theta))\hat{\sigma}(\theta) = (\varepsilon_{mL} - \tilde{\varepsilon}_L(\theta))\tilde{\sigma}(\theta). \quad (25)$$

These relations are universal in the sense that for any SMP, which may be correctly described by LTE model, the strain/stress storage/recovery profiles measured in the strain controlled SMCs must satisfy (at least approximately) these relations. Their role in the theory of LTE models is analogous to the role of universal relations in the theory of finite elasticity (see [15] and references cited therein). In effect, these universal relationships provide a theoretical basis for the experimental validation of LTE constitutive models. For illustration, the “error” defined as a difference of the left and right hand side of the relation (25)₁ has been computed for the data shown in Figure 2. As it may be seen in Figure 3, these data satisfy the “universal” relation (25)₁ within an error less than 1%. This means that the polymer tested by Liu et al. [10] may be modeled within LTE theory provided that the response functions are determined from the profiles measured in SMCs.

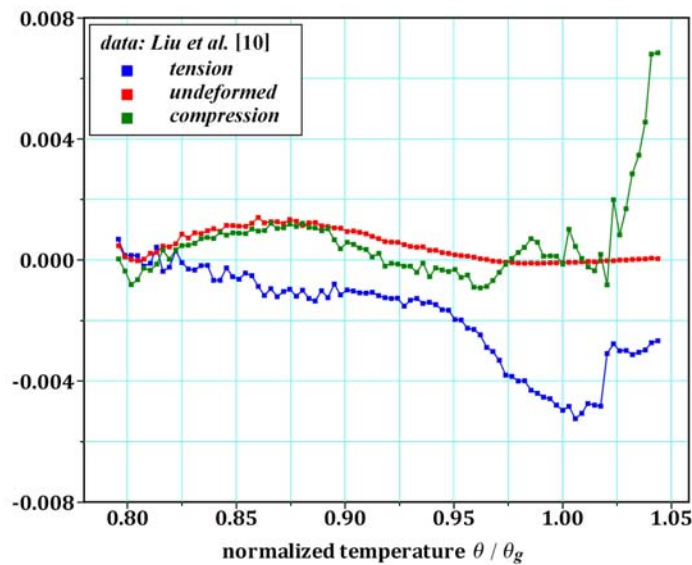


Figure 3. “Error” in the “universal” relation (25)₁ computed from data (Liu et al. [10]) shown in Figure 2.

Though the shape memory cycles discussed above are commonly used to quantify the functional properties of SMPs, most of quantifications are limited to the percentage of shape fixity and the extent of shape recovery under the additional limitation that the deformation temperature coincides with the high temperature. Hence, such tests are not sufficient to fully characterize the functional properties of SMPs. For example, the temperature memory effect which was experimentally observed in some SMPs [5] by performing SMCs with varying deformation temperature across the switching temperature (see illustration Figure 1). Attempts to model this effect within LTE theory and more general theories will be described elsewhere.

7. THERMO-TEMPORAL EFFECTS AND VISCOELASTIC MODELS

The more general test procedures are also required in order to assess the thermo-temporal dependence of functional properties of SMPs, such as the rate of shape recovery, the dependence of shape recovery on creep and relaxation, etc. [6 - 9]. It was also confirmed in studies on the long-term behavior of SMPs that the shape fixity and recovery appear to depend on the strain rates, strain-holding conditions, and temperature rates. Such effects are tested within the “extended” SMCs sketched in Figure 4 (see [3 - 8]),

although no standard method has been established on the overall performance of SMPs for a comparison of one polymer system to the next.

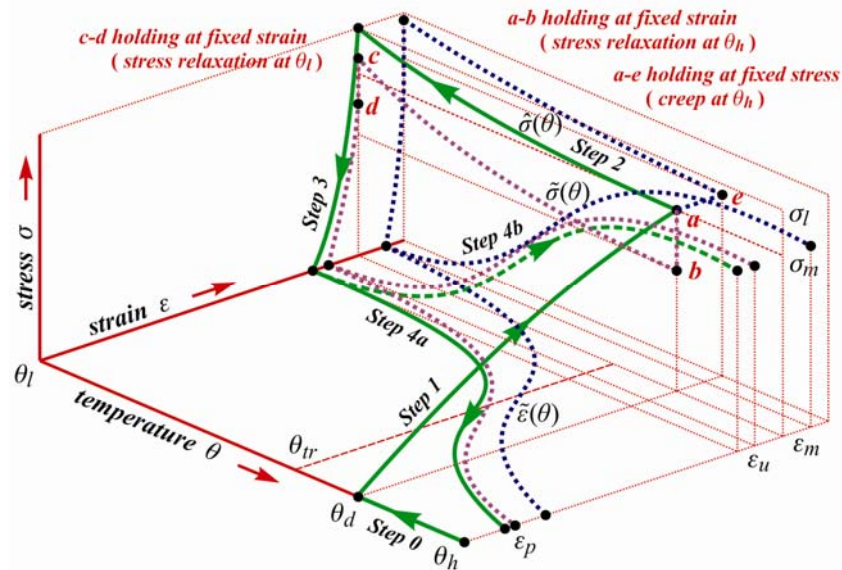


Figure 4. Schematic illustration of the extended SMCs with holding time at high and low temperature allowing for the creep and relaxation of tested samples.

The thermo-temporal dependence of the functional properties of SMPs mentioned above has been successively modeled within the classical rheological models extended to account for the thermal strain and temperature dependent material parameters. For example, it has been shown that a modified Maxwell-Wiechert model consisting of two Maxwell units and a spring can be used to describe different shape recovery kinetics observed for radiopaque polyether urethane (PEU) based 3D substrates under isothermal conditions (see [8]). In a very recent paper, Yu et al. [16] reported that the influence of programming conditions to the free recovery can be unified by a reduced programming time that uniquely determines the shape fixity. They have also shown that using the time-temperature superposition principle, shape recoveries under different thermo-temporal conditions can be extracted from the shape recovery under the reduced recovery time. Their analysis was based on the multi-branch classical rheological model. On the other side, the complete characterization of the functional properties of SMPs under general stress and finite strain states requires far more complex models based on the non-linear theory of thermo-viscoelastic materials (see [8, 9, 13, 14]). Unfortunately, the identification of the relevant response functions and the calibration of a large number of material parameters in such models are problematic and not well-understood.

9. CONCLUSIONS

The three dimensional LTE theory has been formulated which unifies and slightly generalizes a number of models proposed in the literature for SMPs. It is shown that the tensor-valued response functions of this theory are completely determined from the strain/stress storage/recovery profiles measured in the standard strain-controlled SMCs performed in different deformation modes. Moreover, according to this theory, the three profiles measured in the SMCs must satisfy certain “universal” relations. From the presented

analysis it may be expected that the “universal” relations of the LTE theory should have a physical background and they may provide a reliable basis for the study of structure-property relationships.

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